

PATENT SPECIFICATION

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(54) PRODUCTION OF ETHYLENE GLYCOL TEREPHTHALIC ACID ESTERS

(71) We, FMC CORPORATION, a corporation incorporated in the State of Delaware, United States of America, of 633 Third Avenue, New York, State of New York, United States of America, (assignee of LEONARD SEGLIN and JOHN FRANCIS START), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method of producing a light-coloured ethylene glycol terephthalate ester from a grade of terephthalic acid which ordinarily will produce a dark-colored ester.

Terephthalic acid (TPA) for the manufacture of high-molecular-weight polyesters, useful in fiber and film production, is generally produced by the oxidation of p-xylene. A principal problem with the acid so produced is that the technical product obtained by the oxidation contains substantial amounts of color-forming impurities, the principal offender being 4-carboxy-benzaldehyde (CBA). The term "color-forming impurities" as used herein means impurities which are actually colored or materials which can lead to subsequent formation of a colour. It is considered desirable, in producing the best grades of polyester, for the TPA to have a CBA content of less than 25 parts per million (ppm), although acid with 50 to 100 ppm of CBA is considered acceptable for most purposes, and even more may be present if tyre cord is to be produced from the polyester. However, a typical crude TPA will contain a few thousand ppm of CBA, and produce polyesters which are much too highly colored to be commercially acceptable.

In the inception of the polyester fiber industry, crude TPA was converted to the methyl ester, the ester was distilled from the impurities, and the polyester was prepared by transesterification followed by polymerization. Hydrogenation of the impurities sometimes has been used during esterification—see

British Patent Specification No. 955,516—and the esters have been purified by oxidation and crystallization as well; but these roundabout methods have been largely discarded in favor of purification of the TPA to reduce the aldehyde content to an acceptable level.

Recrystallization and oxidation methods have been used to purify TPA without resorting to esterification, but reduction is the favored method. Probably the most desirable technique heretofore employed for carrying out this purification is described in British Patent Specification No. 994,769. The technique involves hydrogenation at high pressures with a hydrogenation catalyst in an aqueous medium. The method is more effective, but unfortunately has economic disadvantages. Because the temperatures are high (about 250°C) and water is present, the reaction vessels require special very expensive materials of construction to resist the combination of high pressure, high temperature and corrosive acid, titanium metal being the preferred material of construction.

In accordance with the present invention there is provided a method of producing light-colored ethylene glycol terephthalate from a crude grade of terephthalic acid which ordinarily produces a dark-colored ester in which the crude terephthalic acid (TPA) and at least 8 times its weight of ethylene glycol are heated together to 160 to 200°C—for a time sufficient to esterify the TPA—generally 60 to 90 minutes—and the esterification mixture, during or after esterification, is reacted with hydrogen at elevated pressures and temperatures—preferably from 10 to 100 atmospheres (measured at room temperature) and from 160 to 200°C, in the presence of a hydrogenation catalyst—most preferably a supported palladium catalyst—for a time sufficient to reduce the aldehyde content to not more than 103 ppm, preferably to less than 25 ppm. After reaction, the catalyst is separated from the reaction mixture, and excess glycol is distilled under vacuum, to produce a white,

[Price 25p]

solid ester which can be polymerized to the desired high-molecular-weight colorless fiber grade polymer.

5 Crude TPA useful in the process of this invention can be produced in many ways which are well known to the art. The methods all involve the oxidation of p-xylene and/or p-toluic acid, using a variety of catalysts. Typical processes are described in British Patent
10 Specifications Nos. 793,192 and 850,536 and in U.S. Patent Specifications Nos. 2,833,816 and 2,853,514. Various oxidizers, such as air, oxygen and nitric acid may be used; and catalysts are conventionally employed. The
15 reaction products are typically isolated from the reaction media, with catalyst removed, and subjected to other treatments to produce a technical grade of TPA which is substantially pure except for the presence of color-imparting
20 impurities at a general level of a few tenths of one percent, typically 2000 to 5000 ppm. Since the principal color-producing impurity is p-carboxybenzaldehyde, color forming impurities are generally reported as ppm of CBA.

25 The technical TPA is then reacted with ethylene glycol, which should be of a grade used for making polyesters; generally, this grade is free of iron and chloride, and is known in the trade as ICF grade (iron and
30 chlorine free).

TPA and ethylene glycol react to form low-molecular-weight esters—such as bis- (ethylene glycol) terephthalate—at temperatures of 180
35 to 200°C. In accordance with this invention, this esterification is carried with at least eight times as much glycol as TPA by weight to ensure a liquid reaction mixture and fast reaction. Optimum handling is obtained at a
40 weight ratio of 10 to 1. Higher ratios of glycol to TPA can be used, but are not desirable because more glycol must be recovered at the end of the process.

45 About an hour is required for the esterification at 200°C, about 1 1/2 hours at 180°C and 3 to 4 hours at 160°C. The esterification can be carried out before hydrogenation, but is most preferably carried out simultaneously. The time may be extended to as much as a
50 full day or more without adverse effects, but since reaction is complete in a much shorter time, there is no reason for extending the reaction time beyond a few hours. The principal adverse effect observed from prolonged
55 heating is formation of a small amount—of the order of a few percent—of diethylene glycol. This formation can be retarded, in known fashion, by the use of very small quantities of alkali—e.g. 0.015% by weight, of
60 sodium carbonate.

The hydrogenation is effected in conventional fashion for hydrogenation, using elevated pressures and temperatures, and a hydrogenation catalyst of conventional type—
65 e.g. a noble metal or finely divided nickel—

care being taken in choice of catalyst that it does not adversely affect esterification. Pressures from 10 to 50 atmospheres have been used, measuring hydrogen pressure at room temperature; higher and lower pressures may be used, but require more expensive equipment and longer times, respectively.

70 Temperatures of hydrogenation may be varied from 160 to 200°C—the top esterification temperature. The preferred catalyst is palladium supported on active carbon or on alumina; hydrogenation time is much shorter than with other conventional hydrogenation catalysts. The amount of catalyst used is not critical, but the rate of the hydrogenation is affected by the amount used. 5 to 25% of catalyst (including support), based on the weight of TPA, is optimum to produce the best grades of product.

75 The esterification reaction can be carried out in one reactor, and then the liquid reaction mixture transferred to a hydrogenator, or the entire reaction can be effected in the hydrogenator. Ordinarily glass-lined or stainless steel reactors can be used, since the temperatures employed are low enough so that corrosion does not occur.

80 After the reaction is complete, the reaction mixture is allowed to cool to a low enough temperature to permit removal of the catalyst by filtration. The ester will separate from the reaction mixture at 60 to 70°C, so that temperatures of the order of 80 to 100°C are desirably used in catalyst separation.

85 The mixture, after catalyst removal, is finally subjected to vacuum distillation, to remove excess glycol. The resulting solid ester is then ready for use in polycondensation to produce fiber and film grade polyester.

90 The ester corresponds roughly to the reaction product of two glycol molecules with a single terephthalate residue (i.e. bis- (ethylene glycol) terephthalate), although there are sometimes present small amounts of higher-molecular-weight material.

95 The following examples demonstrate varying operating conditions under which the process of the present invention is effective.

Example 1.

100 To a 250 ml autoclave was charged 50 g of ICF grade ethylene glycol, 5 g of light yellow TPA containing 2800 ppm of aldehyde (as CBA) and 1 g of palladium on Pittsburgh
105 PCB granula activated carbon as catalyst. The vessel was flushed with hydrogen, pressured to 300 psig, and then heated with rocking agitation. After 3 hours at 195°C, heating was discontinued and the vessel allowed to cool. The reaction mixture was transferred
110 to a glass beaker and heated to 65°C and then to 100°C when filtration was carried out. The filtrate was colorless and of a pleasant odor. Concentration of the filtrate *in vacuo* yielded 8 g of white solid. Polarographic analysis of

the product indicated less than 25 ppm of residual aldehyde.

Data illustrating the effectiveness of other palladium/support combinations are found in the Table.

Example 2.

Example 1 was repeated using an autoclave but a hold time of 1—1/2 hours therein was maintained. The product was colorless and contained 22 ppm of aldehydes.

Example 3.

Ethylene glycol and TPA were esterified using the conditions of Example 1 in 10 to 1 weight proportions over a period of 1—1/2 hours. To 50 ml of the esterification solution was added 0.5 g of palladium charcoal (Baker). The mixture was subjected to reducing conditions as set forth in Example 1, except that 1/2 hour hold time at 200°C was maintained. The colorless product contained 31 ppm of aldehydes.

Example 4.

Ethylene glycol and TPA were esterified at 160°C in 10 to 1 weight proportions over

a period of 4—1/2 hours. For the reduction process, the same apparatus was used as for Example 1. Room temperature hydrogen pressure was 1000 psi, and a hold time of 1/2 hour at 160°C maintained. The colorless product contained 90 ppm of aldehydes.

Example 5.

A scale-up was made in a 1-gallon glass-lined, stirred vessel. To the reactor was charged 200 g of light yellow TPA containing 2800 ppm of aldehydic impurities, 2 liters of ICF grade ethylene glycol, and 25 g of Baker palladium on charcoal catalyst. The reactor was pressured to 500 psig with hydrogen and agitated for 3 hours at 190°C. The reaction mixture was filtered at 100°C to remove catalyst. Excess glycol was stripped from the filtrate *in vacuo*. The white, solid product contained 103 ppm of aldehyde. A sample was polymerized to a hard, white solid.

The following Table shows additional runs carried out in accordance with the procedure of Example 1 but using different support media for the palladium catalyst.

TABLE

Support Designation	Appearance	Residual Aldehyde in Product (ppm)
1A — Columbia SXWC	1/8" pellets of activated charcoal	23
2A — Baker	Granular charcoal (about 1/8")	25
3A — Darco	4 × 12 mesh (U.S. Standard) granules of activated carbon	25
4A — Alumina (Al ₂ O ₃)	1/16" spheres	80

("Columbia" and "Darco" are Trade Marks)

WHAT WE CLAIM IS:—

1. A method for the production of a light-colored ethylene glycol terephthalic acid ester from a grade of terephthalic acid which ordinarily will produce a dark colored ester, which comprises esterifying the terephthalic acid with at least 8 times its weight of ethylene glycol at 160 to 200°C for a sufficient time to obtain the desired ester in solution in the excess glycol, and at some time during or after the course of the esterification hydrogenating the reaction mixture at temperatures up to 200°C and at elevated pressure in the presence of a hydrogenation catalyst for a time to reduce the level of color-forming impurities (as hereinbefore defined) to not more than 103 ppm, separating the catalyst from the re-

action mixture, and then vacuum-stripping excess glycol from the ester.

2. A method as claimed in Claim 1 in which the level of color-forming impurities is reduced to less than 25 ppm.

3. A method as claimed in claim 2 in which the weight ratio of ethylene glycol:terephthalic acid employed is 10:1.

4. A method as claimed in any of claims 1 to 3 in which the catalyst is supported palladium.

5. A method as claimed in claim 4 in which the support is active carbon or alumina.

6. A method as claimed in any of claims 1 to 5 in which 5 to 25% by weight of catalyst is used, based on the weight of terephthalic acid.

7. A method as claimed in any of claims 1 to 6 in which the esterification is carried out at 180 to 200°C.
- 5 8. A method as claimed in any of claims 1 to 7 in which the esterification is carried out for 60 to 90 minutes.
9. A method as claimed in any of claims 1 to 8 in which the hydrogenation is carried out at 160 to 200°C.
- 10 10. A method as claimed in any of claims 1 to 9 in which the hydrogenation is carried out at 10 to 100 atmospheres.
11. A method as claimed in claim 10 in which the hydrogenation is carried out at 10 to 50 atmospheres.
- 15 12. A method as claimed in any of claims 1 to 11 in which the esterification and hydrogenation are conducted simultaneously.
13. A method as claimed in any of claims 1 to 12 in which the catalyst is separated from the reaction mixture at 80 to 100°.
- 20 14. A method as claimed in any of claims 1 to 13 in which the terephthalic acid employed is substantially pure except for the presence of color imparting impurities.
15. A method as claimed in claim 14 in which the color imparting impurities are present in an amount of 2000 to 5000 ppm.
16. A method as claimed in any of claims 1 to 15 in which the ethylene glycol employed is ICF grade.
- 30 17. A method as claimed in any of claims 1 to 16 in which the heating during esterification is performed in the presence of 0.015% by weight of alkali.
18. A method for the production of a light colored ethylene glycol terephthalate ester according to claim 1 substantially as hereinbefore described with particular reference to any of the foregoing Examples.
- 35 19. A light colored ethylene glycol terephthalate ester whenever produced by a method as claimed in any of Claims 1 to 18.
20. Ethylene glycol terephthalate ester polymers whenever obtained by polymerization of an ester as claimed in claim 19.
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